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Impact of NaOH on the Hydrothermal Oxidation of Guaiacol for the Production of Value-Added Products

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Abstract: In this study, the impact of NaOH on the hydrothermal oxidation of guaiacol was investigated. It was found that NaOH significantly accelerated the production of formic acid and acetic acid with H_2O_2 or CuO as the oxidant. With the strong oxidant, H_2O_2, the highest acetic acid yield (15.73%) and formic acid (5.64%) were obtained at 300 °C for 90 s with NaOH 1.0 mol·L^{-1} and a 100% H_2O_2 oxygen supply. In comparison, with CuO as the oxidant, the highest values of acetic acid (13.42%) and formic acid (4.21%) were acquired at 250 °C for 6 h with NaOH 1.0 mol·L^{-1}. Formic acid and acetic acid were generated through the oxidation of intermediates, such as levulinic acid, fumaric acid, maleic acid, etc. These results demonstrated that NaOH catalytic hydrothermal oxidation has potential for the production of value-added chemicals from biomass materials. When CuO is used as the oxidant, this process could also be used as a green method for copper smelting along with the utilization of lignin biomass.

Keywords: hydrothermal oxidation; guaiacol; NaOH; formic acid; acetic acid

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1. Introduction

Biomass conversion has received increasing attention due to the vast demands for chemicals and fuels by humankind. More importantly, this process is both sustainable and largely CO_2 neutral. In fact, biomass conversion has become a research hotspot, because lignin accounts for about one third of the total lignocellulosic biomass [1]. Unfortunately, lignin is generally considered the most difficult component to utilize, because it contains an abundance of aromatic rings with hydroxy and methoxy substituents. Due to the complexity of lignin, the model compound has always been studied to obtain insights into its potential degradation pathways. Guaiacol (2-Methoxyphenol) presents the simplest chemical model for the study of the important structural features of lignin; however, few works related to the oxidation of guaiacol have been performed [2,3]. Yong et al. investigated the oxidation behavior of guaiacol under hydrothermal conditions [4], while Sasaki et al. studied the main products after hydrothermal oxidation, which were catechol, phenol, and o-cresol [5,6]. Additionally, Suzuki et al. reported on the produced small-molecule carboxylic acids, such as formic acid and acetic acid [7]; however, the detailed mechanism of guaiacol oxidation is currently much less explored.

Hydrothermal oxidation enables the decomposition of a variety of types of biomass and is considered to be a promising energy-conversion technology [8] and extensive studies in the hydrothermal reactions of biomass conversion have been conducted [9–11]. Jin et al. reported that small molecule carboxylic acids could be generated from lignin under hydrothermal conditions [12]. Meanwhile, formic acid could be used for hydrogen production. Recently, formic acid was utilized in power fuel cells in automobiles [13]. Acetic acid could be used for the production of industrial chemicals, which are produced mainly from the petrochemical process; however, if lignin could be readily and efficiently utilized, this process would be more promising. It has been reported that NaOH could be used in hydrothermal oxidation as a homogeneous catalyst [14]. Moreover, several studies on the

oxidation of organic compounds have also proven the catalytic effects of NaOH [15,16]. OH^- is considered an initiator or promoter that abstracts a proton from a hydroxyl group and the presence of NaOH impacts not only the reaction efficiency but also the selectivity of oxidation reactions; however, there is less information of the catalytic effects of NaOH.

In the hydrothermal oxidation process, lignin is oxidized to intermediates and small molecular carboxylic acids; therefore, if the reduction of the oxidant could be utilized for chemical production, a hydrothermal reaction would be more beneficial. In our previous study, we studied the reduction of CuO under hydrothermal conditions by guaiacol with NaOH at a mild temperature of 250 °C [17]. It was found that after the reaction, the products included Cu metal and carboxylic acids, such as maleic, fumaric, formic, and acetic acids. Consequently, hydrothermal oxidation could also be used in the copper-smelting process.

In this study, the impact of NaOH on the hydrothermal oxidation of guaiacol, a model lignin compound, was explored. Experiments were performed with NaOH as a homogenous catalyst to verify the acceleration performance. Additionally, experiments with CuO as the oxidant were also conducted. Meanwhile, a hydrothermal oxidation pathway of guaiacol was proposed.

2. Experiments

2.1. Materials

The guaiacol was bought from Wako Pure Chemical Industries, and was chosen as the test material. The H_2O_2 solution, (Hydrogen Peroxide, 30%), CuO (AR), formic acid (AR), acetic acid (AR), and other chemicals were acquired from Sinopharm Chemical Reagent, China.

2.2. Experimental Methods

The experiments were conducted in a batch reactor, made of stainless-steel SUS 316 tubing. The inner volume was 5.7 mL. H_2O_2 was selected as the oxidant for some experiments. The amount of additional H_2O_2 was calculated based on the stoichiometric demand for the complete oxidation of the raw materials. It was assumed that 1 mol of H_2O_2 gives 0.5 mol of O_2. The water fill rate was about 30%. The water fill rate was defined as the volumetric rate of the reaction mixture to the holding capacity of reactor. The schematic of experimental system was shown in Figure 1. Details of the typical reaction procedure can be seen elsewhere [12,18].

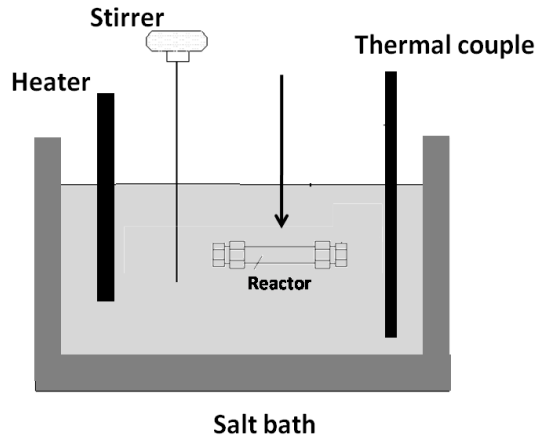

Figure 1. Schematic of experimental system.

When CuO was used as the oxidant, the experiments were performed in a Teflon-lined reactor in an oven. The inner volume was 28 mL. The temperature varied from 200 to 250 °C. The reaction time was from 4 to 12 h. The NaOH concentration was 0.1~1.0 mol/L; the molar ratio of guaiacol to CuO was 1.0 and the water filling was 35%. A 200 mesh CuO powder was chosen in this study. In a typical procedure, 2.5 mmol of CuO powder,

guaiacol and a NaOH-water mixture of 8.0 cm^3 providing 35% water filling were placed into the reactor. Then, the reactor was stored in the oven which was heated to the desired temperature. After some time, the reaction was finished and the reactor was cooled to room temperature. Then, the liquid and solid samples were analyzed.

2.3. Product Analysis

A high performance liquid chromatography analysis of the liquid samples was adopted to investigate the yield of acid. GC-MS was selected for exploring the information of the intermediates. The detailed analysis method information is available elsewhere [19–21].

The acid yield was defined as follows:

$$\text{Yield} = \frac{\text{carbon in formic or acetic acid (g)}}{\text{carbon in initial test material (g)}} \times 100\%$$

3. Results and Discussion

3.1. Experiments with H_2O_2 as the Oxidant

The effects of the experimental parameters, including the NaOH concentration, temperature, time, and additional H_2O_2 amount, on the hydrothermal oxidation of the guaiacol were investigated. Firstly, the experiments were performed with a NaOH concentration from 0 to 2.0 mol·L^{-1} with a 100% H_2O_2 supply at 300 °C for 90 s. As shown in Figure 2, the alkaline concentration, apparently, significantly influenced the acetic acid yield compared to that of the formic acid. The yields of formic acid and acetic acid remarkably increased by varying the NaOH concentration from 0 to 1.0 mol·L^{-1}. The yields slightly decreased with a surplus NaOH addition. In our previous studies, it was reported that alkalis can prevent carboxylic acids from being oxidized [22], which means that the formation of acids would accumulate when the further oxidation was inhibited by adding alkalis. It had been proposed that the addition of alkali may influence the reaction mechanism [17]. Unfortunately, the detailed effect of an additional alkali is now unclear. In this study, these results show that the addition of alkali accelerated the generation of carboxylic acids.

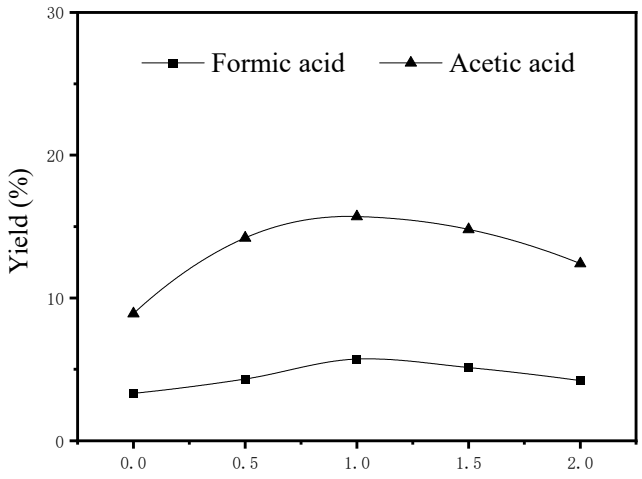

Figure 2. Effects of NaOH concentration.

As we know, temperature is an important factor for hydrothermal reactions. The experiments were carried out with a temperature from 260 to 320 °C and a 100% H_2O_2 supply and NaOH 1.0 mol·L^{-1} for 90 s. As shown in Figure 3, as the temperature increased from 260 °C to 320 °C, the yields first increased and then decreased. These results suggest that the produced carboxylic acids would be decomposed under a higher reaction temperature. The GC-MS chromatogram of the sample with a methyl esterification method is provided in the supporting information (SI). The small molecule acids include propanoic acid, fumaric acid, levulinic acid, butanedioic acid, and maleic acid. In addition, above the optimal

temperature, the decrease in yields of the small molecule acids could be attributed to the acceleration of the decomposition reactions of the small molecule acids with an increase in the temperature.

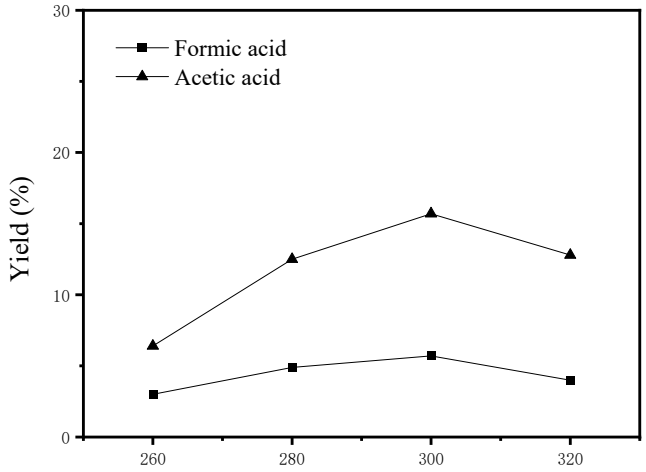

Figure 3. Effects of reaction temperature.

Figure 4 illustrates the effects of the variations in the reaction time with a 100% H_2O_2 oxygen supply and NaOH 1.0 mol·L^{-1} at 300 °C. As shown in Figure 4, the generation of carboxylic acids gradually increased when the reaction time was extended; however, the yield decreased slightly when the reaction time increased from 90 to 120 s, while the formic acid yield increased continuously, until it was almost stable. The highest acetic acid yield was obtained with 15.73% for 90 s. The effect of the reaction time on the variation trend of the formic acid yield was different with that of the acetic acid. The reason for this may be that the production of acids is due to different pathways. On the other hand, acetic acid is more stable than formic acid under alkali-added hydrothermal reactions [19].

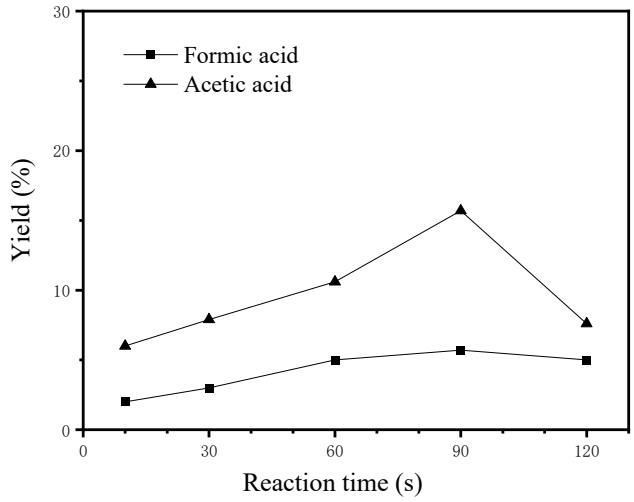

Figure 4. Effects of reaction time.

H_2O_2, which is commonly used as a strong oxidant, decomposed to free radicals under hydrothermal conditions. In this situation, the suitable additive rate of the H_2O_2 addition was very important. Figure 5 presents the effects of H_2O_2 on the yields of acid with NaOH 1.0 mol·L^{-1} at 300 °C for 90 s. The additive rate of the H_2O_2 supply varied from 40% to 120%. The highest yield of acetic acid was 15.73% with an additive ratio of the H_2O_2 of 100%. The yields were lower with a H_2O_2 supply of 40%. The reason for that was that the initial stage of the reaction process mainly resulted from the decomposition of bigger

molecules. While increasing the additive ratio of the H_2O_2, the intermediates, such as the produced carboxylic acids, were further oxidized; therefore, more formic and acetic acid were produced. Meanwhile, the excessive additive ratios of the H_2O_2 also caused the oxidation of the produced carboxylic acids; thus, their yields decreased.

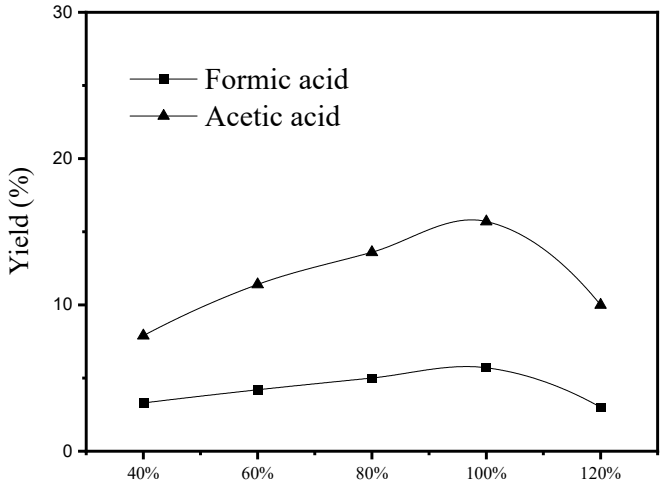

Figure 5. Effects of H_2O_2 supply.

3.2. Experiments with CuO as the Oxidant

Experiments were conducted with CuO as the oxidant to investigate the impact of NaOH on the hydrothermal oxidation of guaiacol with a weak oxidant. The results are shown in Figures 6 and 7.

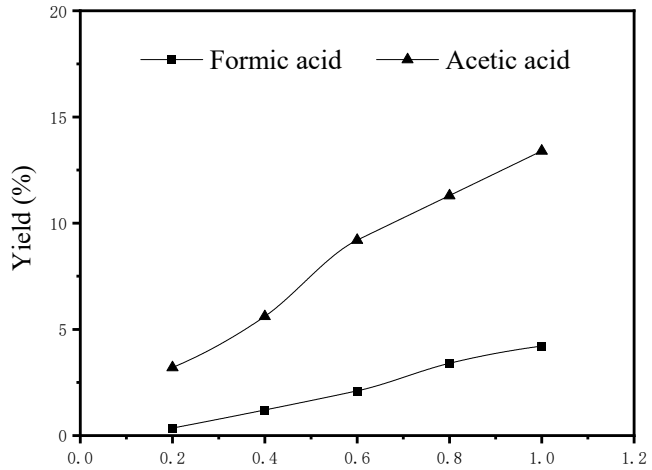

Figure 6. Effects of additional amount of NaOH (guaiacol: 2.65 mmol; 250 °C; 6 h).

Compared with the results obtained using the strong oxidant, H_2O_2 at 300 °C, the reaction time was very long with CuO at 250 °C. When H_2O_2 was used, 1~2 min were enough to finish the reaction; however, the CuO needed 4~6 h at 250 °C. Of course, the reaction temperature was an important influencing parameter; however, the reaction with the H_2O_2 took place very quickly. As shown in Figure 4, the reaction with the H_2O_2 finished almost within two minutes. As shown in Figure 6, when the NaOH concentration varied from 0.2 to 1.0 mol/L, the acid yields significantly increased, suggesting that the addition of NaOH favored the carboxylic acids formation. The reason for this may be that the NaOH tended to influence the decomposition of the carboxylic acids; therefore, the yields of the carboxylic acids increased with a higher NaOH concentration.

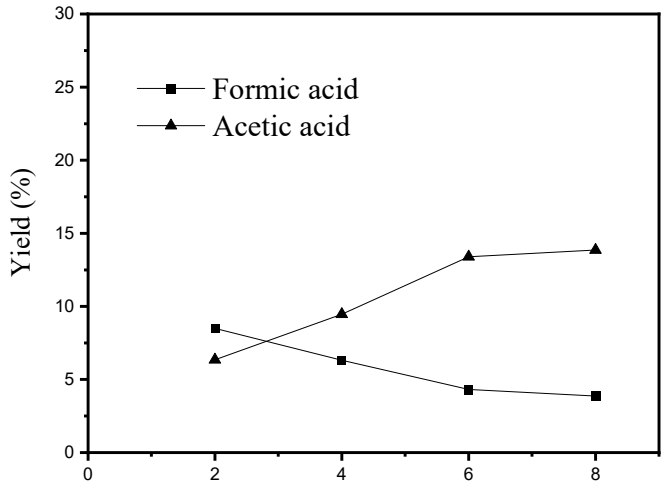

Figure 7. Effects of additional amount of NaOH (guaiacol: 2.65 mmol; 250 °C).

The effect of the reaction time was examined by varying the reaction time from 2 to 8 h. Interestingly, the yield of the acetic acid gradually increased when the time extended from 2 to 8 h, while the generation of formic acid decreased in the process (see Figure 7). In our previous study, we reported on the reduction of CuO with guaiacol in the presence of NaOH [17]. It was found that a higher efficiency of CuO reduction was obtained with a higher NaOH concentration, and also that the carboxylic acids production contributed to the CuO reduction. It should be noted that the yield of the acetic acid increased because the acetic acid was prevented from being oxidized due to the existence of an alkali; however, due to the reducing characteristics of formic aid, which can reduce CuO by aldehyde, the generation of formic acid decreased. Therefore, the variation trends of the yields of acetic and formic acids were different.

3.3. Proposed Reaction Pathways

It is very difficult to understand the reaction mechanisms of the hydrothermal oxidation of guaiacol using in situ detection methods; however, we can analyze the reaction intermediates by analyzing the samples to conclude the possible reaction pathway. From the analysis shown in Figures S1 and S2 (in SI), we found some information about the intermediates. Products, mainly small molecule carboxylic acids, were formed, including propanoic acid, fumaric acid, maleic acid, levulinic acid, butanedioic acid, etc. There was very little information to confirm the exact pathway for phenolic-compound hydrothermal oxidation. Based on our previous study on the reaction pathway, the proposal pathways are shown in Figure 8. As shown in Figure 8, the formation of formic acid and acetic acid mainly comes from the intermediate chemicals, such as unsaturated dicarboxylic acids; however, the detailed reaction pathway still needs more information to be verified.

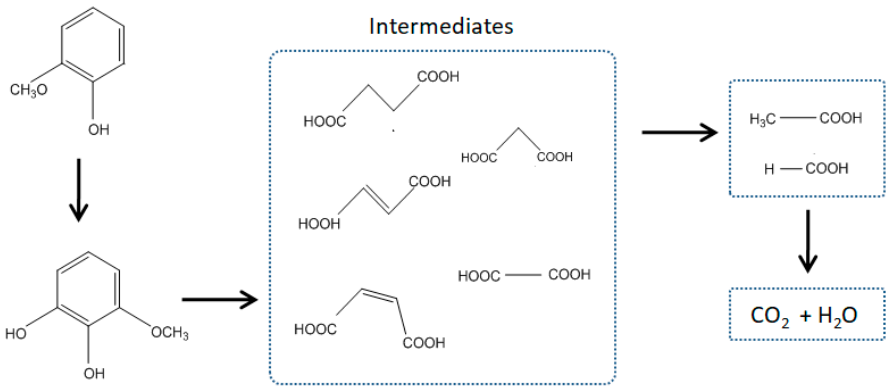

Figure 8. Proposal reaction pathway of guaiacol oxidation under hydrothermal conditions.

By comparison, the reaction process with CuO was very different with the H_2O_2 reaction, which mainly took place in the presence of a hydroxyl radical. Because the hydroxyl radical possessed strong oxidative stress, the H_2O_2 induced the fast oxidation of the guaiacol, resulting in higher organic acid contents. In our previous study, a possible reaction pathway with CuO and guaiacol was proposed [17]. Firstly, catecholate and methanol were produced due to the decomposition of guaiacol. In this process, veratrole can be formed. Then, the CuO was reduced into Cu_2O by the catecholate. O-quinone may have been oxidized by the CuO, producing dicarboxylates, such as muconate, methylsuccinate, succinate, oxalate, and CO_2; therefore, the CuO or Cu_2O were reduced by dicarboxylates.

4. Conclusions

In this study, the impact of NaOH on the production of value-added products from guaiacol under mild hydrothermal conditions was investigated. It was found that NaOH significantly accelerated the production of carboxylic acids with H_2O_2 or CuO as the oxidant. With the strong oxidant, H_2O_2, the highest acetic acid yield (15.73%) and formic acid (5.64%) were acquired at 300 °C for 90 s with NaOH 1.0 mol·L^{-1} and a 100% H_2O_2 oxygen supply. In comparison, with CuO as the oxidant, the highest values of acetic acid (13.42%) and formic acid (4.21%) were acquired at 250 °C for 6 h with NaOH 1.0 mol·L^{-1}. Based on the detection of intermediates, possible reaction pathways were discussed. The formic acid and acetic acid were formed due to the oxidative decomposition of intermediate products, such as butanedioic acid, levulinic acid, maleic acid, fumaric acid, etc. The saturated dicarboxylic acids and glutaconic acid are easier to generate than acetic acid and these results suggest that NaOH catalytic hydrothermal oxidation has the potential for use in the generation of value-added products using biomass materials. In addition, when CuO is used, this process could be used as a green method for copper smelting along with the utilization of lignin biomass.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15218039/s1, Figure S1: HPLC chromatographs of the sample after hydrothermal oxidation. Figure S2: GC/MS chromatogram of the sample after hydrothermal oxidation.

Author Contributions: Conceptualization, X.Z.; methodology, X.Z.; software, X.Z. and G.Y.; validation, X.Z.; investigation, X.Z.; writing—original draft preparation, X.Z. and Y.Z.; writing—review and editing, X.Z. and J.Z.; supervision, J.Z. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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